The Role and Economics of Nano-Graphene Functionalization in Oil Industry Improvement

Amarachi U. Nkwoada¹, Chijioke M. Amakom² and Emeka E. Oguzie¹

¹Department of Chemistry, Federal University of Technology Owerri, Nigeria.
²Department of Physics, Federal University of Technology Owerri, Nigeria.

Authors’ contributions

This work was carried out in collaboration between all authors. Authors AUN and EEO designed the study, wrote the protocol and managed the literature searches. Authors AUN and CMA anchored the field study, gathered the initial data and performed preliminary data analysis. Authors AUN and CMA interpreted the results and produced the initial draft. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOPACS/2016/39683

(1) Natt Makul, Assistant Professor, Department of Building Technology, Faculty of Industrial Technology, Phra-anakhon Rajabhat University, Thailand.
(2) Ali Arvani, University of Missouri-Columbia, USA.
(1) Sandeep Rai, Shriff S.R, Rotary Institute of Chemical Technology, India.
Complete Peer review History: http://www.science-domain.org/peer-review/history/23472

Received 26th November 2017
Accepted 20th February 2018
Published 6th March 2018

ABSTRACT

The toxic pollutants released from oil and gas activities typically takes years of clean-up and reclamation. Hence, creating the need for new nanomaterials that can function as adsorbents, filter membranes, and coating materials, which offer a molecular level of control in separating relevant pollutant mixtures. The advances in graphene-family and its derivatives has proven its effectiveness to gradually replace conventional filter membranes, coatings, adsorbents, sensors for nanomaterials applications in the oilfield. The functionalization of graphene and graphene oxide has enabled such nano-graphene-composite materials to be tailored to meet the new development of coatings, adsorbents, filter membranes and sensors for oil and gas applications with high scalability potentials.

Keywords: Nano-graphene, composite material; graphene oxide, oilfield.

*Corresponding author: E-mail: chemistryfrontiers@gmail.com.
1. INTRODUCTION

The absence of a unified internationally accepted regulation for the oil and gas industry has allowed variations in national policies and directives over the years. Consequently, pollution damages arising from oil industry activities are been addressed differently by national instruments [1]. In Nigeria for instance, the 1990’s oil spill in (Ogoni-land) Niger Delta has other hand, the application of unconventional drilling activities of horizontal and hydraulic fracturing in the U.S has already raised environmental concerns on air quality and groundwater chemistry due to some detected toxic compounds [4,5]. Conversely, in the Gulf of Mexico, the existing lingering spatial clusters of blowouts, explosions, leaks and spills are some potential environmental hazards yet to be abolished [6]. Additionally, the global climatic impact of gas flaring from gas production also remains feral and undocumented to a large extent [7,8]. Thus gas flaring, occasional spills and leaks, produced water, refinery wastes all contribute to environmental pollution. However, pollutants from refining and usage of lower grade oil [9] and automotive combustion emissions are occurrences with the harmful potential to man and environment [10].

As a result, researchers have correlated increased levels of CO$_2$ to combustion emissions and linked to global warming; a subject of debate till date [11]. Nevertheless, oil and gas pollutant emissions and discharge have remained an area of research challenge to both auto manufacturers and oil and gas industries. Although auto-manufacturers have made significant progress in engine and exhaust catalytic designs. The capture and separation of CO$_2$ from flue gases or exhaust emissions remain challenging to both industries [10,12]. Moreover, the large-scale corrosion damage and scaling of oil pipelines and platforms costing over $2.3$ billion annually [13-17] has created the need for materials with high selectivity, tuneable surface chemistry, operating within a temperature range, stable within the operating conditions and performing in the presence of water vapour, other acid flue gases, and be of very low cost. Hence, research has sought solutions towards the investment of materials like steel and their coatings when exposed to the different corrosive environment [18-20] and in corrosive substrates like produced water [21-23]. Thus, several corrosion inhibitors in the oilfield market have emerged over the years with some significant results [24-27]. Hence, the call for nano-materials that is cheaper and environmentally adaptable to the oilfield conventional applications. Such nano-materials would be able to perform as adsorbents for toxic pollutants, corrosion resistant coatings, sensor application for emissions in the oilfield. Subsequently, graphene and graphene derivatives have shown its robustness and versatility to replace traditional materials in both industrial and field practice.

2. GRAPHENE SYNTHESSES AND FUNCTIONALIZATION

Graphene is a type of graphite material with one or many atomic layered graphite using SP$^2$ hybridized honeycomb lattice and having unusual two-dimensional structure. The engineering properties include, good sorption properties, large surface area, good thermal properties and good mechanical strength and high electron transfer and can be synthesised into graphene oxide, nanosheets and nano-composite materials [28,29]. Graphene oxide (GO) is an oxidized derivative of graphene possessing at its basal planes and edges various functional groups and creating intersperse carbon layers with oxygen molecules which have been reduced to separate the carbon layers into separate few-layer graphene [30]. They can be obtained by exfoliating graphite oxide using mechanical stirring or sonication [31,32]. Graphite oxide (GRO) is non-stoichiometric and obtained by graphite oxidation that creates layered structure and interlayer spacing of up to 6.5 A and re-arrangement of hydrophobic graphite into hydrophilic graphite oxide [33]. The increase in interlayer lattice spacing moves from 0.335 nm for graphite to more than 0.625 nm in graphene oxide. Graphene oxide was first synthesized by Brodie in 1859 by adding KClO$_3$ to a mixture of graphite in concentrated HNO$_3$. Staudenmaier in 1898 used concentrated H$_2$SO$_4$ and HNO$_3$ and chlorates to produce highly-oxidized graphite oxide while Hummers in 1958, oxidized graphite by treatment with KMnO$_4$ and NaNO$_3$ in concentrated H$_2$SO$_4$ [34]. Hence, graphene functionalization confers an improvement in syntheses of nano-material properties required for adsorption of gases, storage, separation and sensors [30]. For instance, aminated graphene oxide used for CO$_2$ adsorption increases polarization and are remarkably reversible reactions [34,35]. The functional groups responsible for this, create reactive sites with several surface-modification reactions that
enable functionalized graphene oxide and nano-graphene based materials to be tailored to ‘specifics’. Thus varying the concentrations of surface functional groups and the material band gap, the work function of graphene oxide/nano-graphene composites can be tuneable to offer reactive sites for adsorption of gaseous pollutants (CO, CO₂, NO, NO₂, NH₃), removal of inorganic pollutants (heavy metal ions) and adsorption of organic pollutants (PAH, VOCs, unburnt hydrocarbons and gasoline emissions) [29,36,37,38]. The common functionalization approach as reported by researchers was expressed in Table 1 [39-64].

Thus this functionalization process can be simplified in the sketch in Fig. 1 above. The graphite powder/flake in stage 1 is oxidized by these surface active reagents in stage 2 and thereafter exposed to certain temperature program in stage 3 for pore formation and creation of reactive site/functional groups. The oxidized surface-active material confers certain specific properties on the new material (honeycomb structure) which would then be characterized for specific applications. Hence heavy metal removal and gas adsorption are achieved through several syntheses routes as shown in Table 1. In Table 1, it represents functionalization and applications of graphene/graphene oxide in the industry. This includes synthesis of nano-graphene/graphene oxide, adsorption of heavy metals, gas adsorption and water treatment. From the table, the common precursors were graphite flakes and graphite powder, while Zn, Pb, Ni, Cu and Cd are the common adsorbates. The use of more sensitive instrumentation like ICPAES/OES for adsorption studies were reluctant. Moreover, the use of routine laboratory oxidizing reagents (NaNO₃, H₂SO₄, KMnO₄, HCl) etc. were prevalent. Hence, the inter-conversion between hydrophobic graphite and hydrophilic graphene oxide has led researchers to pursue its intercalation ability when immersed in solvents [66,78]. Consequently, this 2D material through chemical vapour deposition, exfoliation, and hydrothermal synthesis can be tailored to meet a new generation of nano-materials for oil and gas applications [79]. The nano-material development lays emphases on the chosen graphite precursor which ultimately affects the performance of such materials [80]. Structural studies using AFM, XRD, SEM, TEM, Raman spectroscopy and photoluminescence spectroscopy have shown that by adding functional groups to the GO, both chemical and physical properties can be tuned even as induced defects or impurities. Thus this nano-graphene and composite graphene materials can similarly be studied by first-principles calculations as observed in transition metal dichalcogenides [81-83]. Moreover, nano-graphene synthesis and application as selective material are enhanced by GO/GrO/rGO interconversion capability [66-77].

Conversely, three flaws were demonstrated during graphene synthesis. Surface functionality weakens the platelet interactions due to the hydrophilic nature, the use of sonication process through faster than mechanical stirring causes irregular size distribution, while oxidation
fragments the graphite and introduces impurity and structural damage. However, its scalability potential as mono or polydisperse layers are boundless [84, 85] with potential nanocomposite material applications in the oilfield applications.

The interpretation of Table 1 was represented in Fig. 2. The Fig. 2(A) showed that the reagents on the right are the frequently used reagents during synthesis and preparation of graphene/graphene oxide.

### Table 1. Methodologies of graphene preparation and synthesis

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Reagents</th>
<th>Instrumentation</th>
<th>Adsorbent</th>
<th>Adsorbate Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Powder</td>
<td>NaNO$_3$, H$_2$SO$_4$, KMnO$_4$, HCl, H$_2$O$_2$</td>
<td>UV/Visible, FT-IR-ATR, XRD, XPS, SEM</td>
<td>Graphene Oxide</td>
<td>Mn</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>NaNO$_3$, H$_2$SO$_4$, KMnO$_4$, H$_2$O$_2$, KCr</td>
<td>UV/Visible, XPS, SEM, XRD Raman Spec, TGA</td>
<td>Graphene</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite Flakes</td>
<td>KMnO$_4$, H$_2$SO$_4$, H$_3$PO$_4$, C$_2$H$_5$OH, HCl</td>
<td>FTIR-ATR, AFM, TGA, NMR, XRD, TEM, XPS</td>
<td>Graphene Oxide</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite Flakes</td>
<td>H$_2$SO$_4$, H$_3$PO$_4$, KMnO$_4$, CO$_2$ Pressure Swing</td>
<td>FTIR, XRD, SEM, TEM,</td>
<td>Graphene Oxide</td>
<td>Gas Adsorption</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>NaNO$_3$, H$_2$SO$_4$, KMnO$_4$, H$_2$O$_2$, HCl</td>
<td>XPS, FTIR, XRD, SEM</td>
<td>GO/Sawdust</td>
<td>Ni$^{2+}$ adsorption</td>
</tr>
<tr>
<td>Graphite Flakes</td>
<td>KMnO$_4$, H$_2$SO$_4$, Na$_2$SO$_4$, H$_2$O$_2$, NaNO$_3$</td>
<td>XRD, TEM, XPS, Raman Spec, UV-visible</td>
<td>GO/Film</td>
<td>GO coatings</td>
</tr>
<tr>
<td>Graphite Flakes</td>
<td>NaNO$_3$, H$_2$SO$_4$, KMnO$_4$, H$_2$O$_2$, HCl</td>
<td>FTIR, SEM, FESEM, Raman Spec, XRD</td>
<td>Graphene Oxide</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite flakes</td>
<td>NaNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, KMnO$_4$, H$_2$O$_2$</td>
<td>TEM, FT-IR, XRD, TGA, UVAvis, XPS, Elemental analyser</td>
<td>Graphene Oxide</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>H$_2$SO$_4$, P$_2$O$_5$, HCl, K$_2$SO$_4$, KMnO$_4$, H$_2$O$_2$</td>
<td>XRD, FTIR, TGA, DSC, TEM, Elemental analyser</td>
<td>GO/Amines</td>
<td>CO$_2$ Adsorption</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>HNO$_3$, KOH,</td>
<td>XPS, SEM, hRTEM, AFM</td>
<td>Graphene Sheets</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite</td>
<td>KMnO$_4$, EDTA, Hydrazine, HCl, Ethyl alcohol</td>
<td>UV/Vis, (GNS@MnO$_2$)</td>
<td>Graphite oxide GrO</td>
<td>Zn$^{2+}$, Ni$^{2+}$, Cr$^{3+}$ &amp; Pb$^{2+}$</td>
</tr>
<tr>
<td>Graphite Flakes</td>
<td>H$_2$SO$_4$, NaNO$_3$, KMnO$_4$, H$_2$O$_2$</td>
<td>TEM, Raman Spec, XPS, UV/Vis, LCAMS, Luminescence Spec</td>
<td>Graphene Oxide</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Pitch Based Carbon Fibre (P-CF)</td>
<td>H$_2$SO$_4$, K$_2$SO$_3$, P$_2$O$_5$, HCl, KMnO$_4$, H$_2$O$_2$</td>
<td>FT-IR, SEM</td>
<td>Reduced GO (P-GO) &amp; Pristine GO (p-GO)</td>
<td>Synthesis</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>HCl, Na$_2$CO$_3$, HNO$_3$, NaOH, NaNO$_3$, KMnO$_4$, H$_2$O$_2$</td>
<td>XRD, Elemental Analyzer, AAS, EDX</td>
<td>GrO</td>
<td>Synthesis Scale up &amp; purification</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>PC$_6$, HCl, THF, NaNO$_3$, DCM, H$_2$SO$_4$, KMnO$_4$</td>
<td>FT-IR, XRD, XPS, SEM and AFM</td>
<td>Graphene Oxide</td>
<td>Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Ni$^{2+}$</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>NaNO$_3$, LiNO$_3$, NaCl, KNO$_3$, KMnO$_4$</td>
<td>FESEM, TEM, TG-DSC, FTIR</td>
<td>Magnetic GO &amp; β-Cu$_2$(OH)$_2$PO$_4$</td>
<td>Cu$^{2+}$</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>H$\text{N}_2$, K$\text{O}_3$,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>H$\text{N}_2$, KO$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref: 94, 84, 85
<table>
<thead>
<tr>
<th>Precursor</th>
<th>Reagents</th>
<th>Instrumentation</th>
<th>Adsorbent</th>
<th>Adsorbate/Route</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite powder</td>
<td>Hummers, Chitosan</td>
<td>TEM, XPS, IR spec</td>
<td>GC-CS aerogel</td>
<td>Cu²⁺</td>
<td>56</td>
</tr>
<tr>
<td>Graphite flakes</td>
<td>NaOH, HCl, KMnO₄, H₂SO₄, NaNO₂, H₂O₂</td>
<td>FTIR, SEM, EDX</td>
<td>PVP-GrO</td>
<td>Cu²⁺</td>
<td>57</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>H₂SO₄, HNO₃, HCl, KCl, Oxalyl &amp; Acyl Chlorides</td>
<td>FAAS</td>
<td>GO-H₂NP</td>
<td>Ni²⁺</td>
<td>58</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>Hummers, NaBH₄</td>
<td>FTIR, Raman, SEM, TGA, XRD, AAS</td>
<td>Reduced GrO</td>
<td>Pb²⁺</td>
<td>59</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>NaNO₂, KMnO₄, H₂SO₄, H₂O₂, HCl</td>
<td>FTIR, TGA, XRD, SEM AAS</td>
<td>Graphene Oxide</td>
<td>Zn</td>
<td>61</td>
</tr>
<tr>
<td>GO purchased</td>
<td>HCl, NaOH, KMnO₄, H₂O₂</td>
<td>FTIR, AAS</td>
<td>GO-G</td>
<td>Zn</td>
<td>62</td>
</tr>
<tr>
<td>Camphor &amp; graphite</td>
<td>H₂SO₄, HNO₃, KClO₃</td>
<td>AFM, ATM, XRD, TEM FTIR</td>
<td>Graphene Oxide</td>
<td>Synthesis</td>
<td>63</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>NaNO₂, NaNO₃, NaOH, KMnO₄, H₂O₂, K₃Fe(CN)₆</td>
<td>SEM, UV-Vis, FTIR, XRD Graphene Oxide</td>
<td>Synthesis</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>Graphite powder</td>
<td>NaNO₂, KMnO₄, H₂SO₄</td>
<td>Undisclosed</td>
<td>MWGO</td>
<td>Pd/GO complex</td>
<td>65</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>H₂SO₄, HNO₃, H₂O₂, HCl</td>
<td>XRD, FTIR, SEM GO/Fe₂O₃</td>
<td>Wastewater treatment</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Graphite powder</td>
<td>H₂SO₄, P₂O₅, H₂O₂, K₂SO₃, KMnO₄</td>
<td>ICP-MS</td>
<td>Fe₃O₄@SiO₂@PANI-GO</td>
<td>REE determination</td>
<td>67</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>H₂SO₄, H₂PO₄, H₂O₂, KMnO₄</td>
<td>XRD, FESEM, XPS, TEM Graphene sheets &amp; CO₂ adsorption</td>
<td>CO₂ adsorption</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Graphite powder</td>
<td>HNO₃, H₂SO₄, hydrogel</td>
<td>AFM, TEM, UV-Vis, DPASV 3DGO</td>
<td>Zn, Pb, Cu, Bi, Cd</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>Natural graphite</td>
<td>Hummers method</td>
<td>TEM, SEM, XPS</td>
<td>rGO</td>
<td>Gas sensor</td>
<td>70</td>
</tr>
<tr>
<td>Graphite powder</td>
<td>H₂SO₄, KMnO₄, NaNO₂, H₂O₂</td>
<td>XRD, TEM, Raman spec Graphene sheets</td>
<td>CO₂</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>Grape Extract</td>
<td>H₂SO₄, KMnO₄, H₂O₂, HCl, NH₃</td>
<td>FTIR, XRD, UV-Vis, TEM GO/Rego</td>
<td>H₂O treatment</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Graphite powder</td>
<td>Hummers method</td>
<td>TGA, SEM, XRD, FTIR Uio-66/GO</td>
<td>CO₂</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>Graphite flakes</td>
<td>Hummers, NaNO₃, (Mn(acac)₂·4H₂O)</td>
<td>TEM, EDX, SEM, XRD, TGA, FTIR, Raman spec GMNO</td>
<td>CO₂</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>Undisclosed Raman Spec, FTIR, TEM, SEM PANI-HEEG CO₂ capture</td>
<td>CO₂ capture</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>Improved Hummers method XRD, SEM, TGA, FTIR HC-TEM, Cu-BTC-GO Gas storage</td>
<td>Gas storage</td>
<td>76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>Hummers method Atomic deposition on PG TM-Graphene CO, NO, O₂ and CO₂ adsorption &amp; sensing</td>
<td>77</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


---

5
This may be an indication of common methodologies that are routinely practised among researchers during synthesis/preparation thus providing the need for research into alternative low cost and effective reagents. The Fig. 2(B) showed that material characterization using XRD and FTIR, SEM and TEM were frequently utilized by researchers in almost all research studies. Hence, information exists about the characterisation of graphene/graphene oxide, albeit not tailored towards oilfield applications. Fig. 2(C) showed that graphite powder was the most common form of graphite used. This may be due to its larger surface area and thus induces faster reaction kinetics. The application of graphene and its nano-composites in Fig. 2(D) showed that the study and application of graphene oxide as adsorbents almost doubled the same activity in coating, gas-sensor and water purification applications. Thus, these suggest that there had been slower growth of the application of nano-graphene and graphene derivatives in sensor application, wastewater purification and oilfield coating utilization. Hence, the need for research into nano-graphene and its composite material applications in oil pollutant removal, sensor development, wastewater purification and other oilfield applications.

3. ADSORBENTS AND SENSORS

Greenhouse gases especially CO₂ are known to cause global warming [86] with consequent pollution and economic losses arising from climatic changes. The losses are projected to be around 5–20% of the global gross domestic product, hence the need for the development of materials that can function as CO₂ adsorbents. The emphasis on such materials [87] are materials that offer a molecular level of control by tailoring their performance in separating relevant gas mixtures. The common adsorbent in Carbon Capture and Sequestration (CCS) for CO₂ separations is the use of microcrystalline porous solids known as graphene. This porous carbon has a well-developed pore size, excellent stability and tuneable surface chemistry, enabling synthesis of nano-graphene materials with defined nanostructure and morphology. They can recover more than 90% of flue gas with CO₂ purity higher than 90% and at a cost more economical than the usual amine adsorption process [88,89,90].

Graphene oxide has the ability to successively regenerate and retain more than 97% of its intrinsic capacity [89,90]. In addition, molecular dynamic (MD) simulations have demonstrated...
that porous graphene can efficiently separate gases according to their molecular sizes [91,92]. Studies from molecular dynamics and density functional theory also showed that when CO$_2$ approaches graphene surfaces functionalized with monodisperse metals, the force is larger than the initial repulsion [93,94]. Consequently, the CO$_2$ molecule is dissociated in two parts C and O. The CO fraction is adsorbed on the material surface in such a way that the C atom is bonded to three metal atoms and the O atom is bonded to another metal atom. Such nano-materials can equally be enhanced into carbon monoxide capture and separation [95,96]. Accordingly, researchers have suggested that the ideal CO$_2$ sorbent must exhibit the following four properties: the material must adsorb and desorb CO$_2$ within a temperature range, the material should exhibit durability and stability within the operating conditions, show high selectivity and must perform in the presence of water vapour, and other acid flue gases and be a low-cost material [97,98,99]. Thus, nanographene and its material composites are well fitted into this material development research and application due to their excellent adsorptive behaviours such as large surface area, good thermal resistance, active surface functional groups and a low-cost material [100,101,102,103].

Graphene and graphene-based derivatives can be synthesized into different nano-composites with specific sensor-adsorptive behaviour [104]. In the event of a gas molecule adsorbing onto the graphene surface, the local change in the carrier concentration induces a doping of the delocalized 2D graphene, which can be monitored electrically in a transistor-like configuration. Graphene has superior electrical conductivity (106$\ \Omega^{-1}\ \text{cm}^{-1}$) nearly transparent in visible light (97.7%), high intrinsic carrier mobility ($2.5\times10^5\ \text{cm}^{2}\ \text{V}^{-1}\ \text{s}^{-1}$), high specific surface area (2630 $\text{m}^2\ \text{g}^{-1}$), excellent mechanical strength (Young’s modulus > 1 TPa), and high thermal conductivity (above 3000 $\text{W} \text{m}^{-1} \text{K}^{-1}$).

These properties reduce the background noise in transport experiment and confers on graphene and its nano-composites an excellent material for gaseous adsorption. In addition, the above-mentioned properties also confer on graphene, field effect transistor ability, electro-chemical mobility, fluorescence, chemiluminescence and colormetric sensors ability [100,105,106,107]. Subsequently, when nano-graphene/graphene derivatives are incorporated into sensor devices, it displays a high ampie sensitivity to detect parts-per-billion levels or even single molecular events at a rapid rate, which have been obtained experimentally. Remarkably, graphene sensitivity is not limited to chemical species, but can be generally applied to any phenomena capable of inducing a local change in the carrier concentration, such as the presence of magnetic field, mechanical deformation or external charges [108,109,110,111]. Additionally, graphene and its nano-composites interact with permanent dipole molecules, while the presence of polar functional groups on graphene surfaces leads to specific interactions with polar molecules, thereby enhancing the overall interaction potential of the surface as an adsorbent and sensor material [112,113].

The effective sensor/adsorbent ability of nanographene/graphene derivatives is because of the well-defined pores of graphene. Graphene has uniform pore sizes that can be tuned from 10 nm to over 10 $\mu$m and the possibility of stacking multiple layers of graphene or nanographene on the selected porous support [114,115]. Wherein the defects in one layer are cushioned by another layer. Also, the Fascination of graphene application in membrane separation of gases has remained desirable due to the low energy cost. Hence, low-cost materials that can adsorb CO$_2$ efficiently will undoubtedly enhance the competitiveness of adsorptive separation for CO$_2$ capture in flue gas applications [120]. Furthermore, graphene/nano-graphene precursors can be obtained from bio-waste and non-bio-waste. Such materials include camphor (C$_{10}$H$_{16}$O), tea tree extract, sesame oil, foods like cookie and chocolate, waste products: (grass, plastic, dog faeces) insect-derived vegetation animal wades: (bone and cow dung), solid plastic waste etc [121]. Thus, the continued development of graphene and graphene nano-composite materials is necessary to achieve adsorbents/sensors that will result in the decrease of overall costs and greenhouse emissions compared to other conventional materials like amine based adsorbents [122,123,124] through syntheses and functionalization.

4. OILFIELD AND COATING

One of the critical focus in nanotechnology applications in the oil and gas industry has been fluid loss control and rheology [125]. For instance, the additions of graphene oxide to bentonite and xanthan has shown to remarkably
affecting fluid loss control, thermal stability and loading effectiveness even at low levels of 2-5 pounds per barrel [126]. They can then be tuneable for stabilization and cementing [127], thereby improving interfacing adhesion [128] due to graphene oxide hydrophilic nature. Graphene coatings provide water and oil resistance, hence a promising anti-corrosion material [129]. Moreover, dispersing graphene/graphene oxide in polymer matrices induces \(\pi-\pi\) interactions of the \(\pi\)-conjugated graphene basal planes and the aromatic moieties on the backbone of the polymer which aids passivation of metal surfaces [130,131].

For instance, melamine sponge coated with graphene has shown higher oil-absorption capacity up to 80 g/g [132]. On the other hand, lubrication is required to improve movement of machine parts. Subsequently, ultrathin graphene prepared by exfoliation of graphite oxide focused on solar radiation gave significant improvements in frictional characteristics, anti-wear, and extreme properties compared to base oil [133]. Graphene and MoS\(_2\) dispersed in esterified bio-oil as lubricants for steel as additives were observed to reduce friction coefficient and wear of the steel samples up to load of 300 N and the rotational speed of 850 rpm [134]. Furthermore, it can also be blended to produce nano-filter membranes employed to reduce membrane fouling and prevent blockage of the wastewater treatment system in refineries [135]. Also, graphene aerogel dispersed into crude oil solution after adsorption reduced concentration.

Graphene/graphene oxide adsorption capacity determined to be 169 mg/g [136] was placed under continuous vacuum regime, had an adsorption capacity of 28 L of oil per gram of aerogel [137]. Hence, the graphene aerogel was ascribed as cost-effective material for oil spill clean-up and water purification applications.

On the other hand, the applications of physical and chemical processes have dominated oil industry for wastewater, refinery treatment and drilling processes. However, the emergence of membrane distillation, ultrafiltration, microfiltration, nano-filtration and reverse osmosis with a carbon precursor and nano-composite materials have proven to be more viable than tradition techniques [138,139,140,141,142]. For example, research has shown that using Fe\(_2\)O\(_3\) nano-particles and carbon nanotubes increased the removal of emulsified oil from water [143]. Also, carbon foam nano-composites has shown promising fate in oil/water separation [144] as well as carbon fabrics designed with carbon nano-tubes [145]. Additionally, soil sorbents are also reported to be removed by biodegradable polyactic acid infused with reduced graphene and graphene oxide [146].

With this in mind, it can then be observed that recent advances of the graphene family have proven its efficiency in the removal of toxic pollutants from wastewater [147], oil spill clean-up [148,149], and produced water treatments [150]. In addition, selective gas-water-oil separations [151] and post-combustion \(\text{CO}_2\) capture [152,153] have recorded similar progress in the oil industry using graphene/graphene oxide nano-composite materials. Although, graphene/graphene oxide advancement as corrosion and coating materials [154-158] has recorded significant progress, albeit at a slower pace compared to adsorption applications. However, the functionalization of graphene/graphene oxide and its nano-composite materials provides promising cheaper and efficient approach that could progressively replace traditional materials [25,40,44,67,159,160,161] in oilfield applications.

5. OUTLOOK

The review study conducted had already identified graphite powder as the most common precursor for nano-composite synthesis for synthesis/preparation methodologies were often taken by researchers leading to overutilization of common reagents and materials. These reagents can be seen in Figs. 1 & 2.

On the other hand, more information exists about the characterisation of graphene/graphene oxide albeit not tailored towards oilfield applications. Graphite powder was the most common form of graphite used and may be limiting graphitization of waste materials for graphene/graphene oxide applications. Studies also showed that the study and application of graphene oxide as adsorbents doubled the same activity in any of coating, gas-sensor and water purification application. Thus it depicted they slow growth of graphene and graphene oxide utilisations in sensor application, wastewater purification and oilfield coating utilisations. We, therefore, recommend the following.

8
5.1 Graphite

Graphite is the chief material precursor for graphene and graphene derivatives. Research studies on the precursors of graphene and graphene oxide tailored towards sensor development, adsorbents and anti-corrosion coatings in the oilfield should be progressively increased. Because the potential of synthesizing cheap graphene precursors is enormous and easily achievable.

5.2 Synthesis

Knowledge gap exists about how the different concentrations of oxidizing and reducing reagents affect the synthesis of GO/GrO/GO and its inter-conversion of graphene, graphene oxide and graphite oxide. More research studies should be conducted in this area principally towards oilfield applications.

5.3 Functionalization

Little information on studies of chemical equilibria of graphene in different media and how it affects adsorption and corrosion studies for oilfield applications subsists. However, limitless novel oilfield applications are achievable when this principle is well understood. In addition, incorporating thermal effects would be productive since oil platforms also exist in polar and and regions.

5.4 Characterization

Characterization of the nanomaterial (graphene/graphene oxide) with cutting-edge nanotechnology should be performed. This will elucidate basal plane orientation and functionalization of GO/GrO/GO for adsorption and coatings in oilfield applications. Such information will enhance material development for oilfield applications.

5.5 Graphene/Graphene Oxide

With the nature of environmental damages resulting from oil and gas drilling, production and refining, there is a need for nano-materials that are cheap adsorbents, sensors and coating materials. Graphene and graphene oxide materials (composites) seem a progressive material occupying this niche for oil spill clean-up, produced water treatment, selective gas-water-oil separation, post-combustion CO2 capture, corrosion and coating materials. Thus we recommend the functionalization of nanographene/graphene oxide in the oil and gas industry.

6. ECONOMICS OF GRAPHENE/GRAPHENE OXIDE PRODUCTION

Graphene has emerged as the most promising nano-material and also described as the thinnest material on earth with just one atom thickness. At the atomic scale, graphene is a 2D material arranged in hexagonal like bonds, and its unique properties make it the most hyped material with electronic circuits. The growth of graphene market in the oil industry has been hampered by the absence of research into technological potentials of this material as well as the associated cost. However, graphene has found large markets in key industry players such as the electronic, healthcare, automotive, energy and power, aerospace and defense.

For example, the cost of a 50x50 monolayer graphene thin films by Graphene Square is about $263 and further $819 on Cu foil and PET thin film, respectively. While Graphene Nanoplatelets (5-8 nm thick) manufactured by a company such as XG Sciences cost about $ 219-229/kg. This high cost of graphene material is a major obstacle to its adoption for commercial applications worldwide [161,162].

On the other hand, Synthesis of graphene for commercial usage has been classified based on the following: A major activity is directed towards the development of Chemical Vapour Deposition (CVD) and exfoliation techniques. Furthermore, exfoliation methods include (a) mechanical exfoliation of graphite, (b) liquid phase exfoliation of graphite and (c) chemical exfoliation of graphite oxide. Other commonly used dominant techniques are epitaxial growth on SiC substrates, chemical synthesis and unzipping of carbon nanotubes. All the above-mentioned methods have made significant discoveries with potential for scaled-up production of graphene at an affordable cost.

Similarly, academic/research institutes are focussed on creating diverse approaches such as chemical synthesis, electrochemical exfoliation, liquid phase exfoliation, microwave-assisted synthesis and CVD. Some of the key players institutes/Universities making significant impact towards graphene research are National...
Nanomaterials and University of Idaho (Chemical synthesis); Seoul National University and Korea Institute of Science and Technology (CVD); Chinese Academy of Sciences (Epitaxial growth); University of Ulsan, Chonnam National University (Exfoliation technique); Beijing Institute of Junior University and Rine University (Unzipping of CNTs) etc.

Finally, it is worthy of note that multinational corporations such as IBM, Samsung Group, Hitachi Ltd are following the CVD approach to develop high-end optoelectronic products based on the use of high-quality large area graphene thin films.

While on the contrary, the start-up companies such as Nanotech Instruments (Angstrom Materials), XG Sciences, Vorbeck Materials Corporations are directing their efforts towards developing further processing routes from exfoliation and chemical synthesis for the large-scale production of graphene nanoplatelets used for low-end products. Such materials include battery and supercapacitor electrodes, fillers for plastics, sensors, conductive inks and coatings etc. Thus in order to meet the challenges existing in the oil industry, major effort need to be re-directed worldwide by scientific community towards the development of innovative approaches for the production of graphene specifically tailored for coatings, adsorbents/absorbsents and sensors used in the oil industry. The potential and scalability are high due to graphene's thermal conductivity, electrical conductivity, energy storage, barrier strength and mechanical strength [161,162].

7. CONCLUSION

Graphene potential in the oil industry is vast and ever growing. It would be evident from this article that this situation is about to change or may remain regressive due to change in energy shift. The article also outlined the possible directions for future research and it is hoped that future work along these lines would help in industry, enabling them to realize commercialization of graphene products in the oil industry.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


9. Nunes Vas P, Bussotti F, Papini A, Tani C, Domingos V. Pollution emissions from a petrochemical complex and other environmental stressors induce structural...
DOI: 10.1016/j.ecolind.2016.02.054


DOI: 10.1016/j.atmosenv.2015.08.006

DOI: 10.1108/000355901010003

DOI: 10.4236/eng.2011.36078

DOI: 10.1016/j.engfailanal.2015.11.049

DOI: 10.1016/j.engfailanal.2016.05.029

DOI: 10.1016/j.jlp.2015.03.006


DOI: 10.1016/j.corsci.2014.04.044

DOI: 10.1016/j.corsci.2015.08.023


DOI: 10.1016/j.corsci.2016.01.012

DOI: 10.1108/ACMM-12-2015-1622


DOI: 10.1088/2053-5612/2/3/032001

DOI: 10.1016/j.corsci.2014.1.025


40. Plankkio C, Santamaria R, Menendez R. Graphene materials with different structures prepared from the same graphite by the hummers and brodie methods Carbon 2013;65:166-164. DOI: 10.1016/j.carbon.2013.08.009


42. Feng L. Fast adsorption of nickel ions by porous graphene oxide/sawdust composite and reuse for phenol degradation from aqueous solutions Journal of Colloid and Interface Science 2014;436:90-98. DOI: 10.1016/j.jcis.2014.06.065


Shawerai S, Chen B, He M, Hu B, Xiao Z. Determination of trace/ultratrace rare earth elements in environmental samples by ICP-MS after magnetic solid phase extraction with Fe3O4@SiO2/polyaniline-graphene Oxide Composite Talanta. 2014;119:458-466. DOI: 10.1016/j.talanta.2013.11.027


Huang H, Ting C, Liu X, Ma H. Ultrasensitive and simultaneous detection of heavy metal ions based on three-dimensional graphene-carbon nanotubes hybrid electrode materials. Analytica Chimica Acta. 2014;852:45-54. DOI: 10.1016/j.aca.2014.06.010


83. Mechanical properties of graphene and graphene-based. Progress in Materials Science 2017;90:90-128. DOI: 10.1016/j.pmatsci.2017.03.004


DOI: 10.4209/aaqr.2012.05.0132

DOI: 10.1039/c2ee03403d

DOI: 10.1016/j.memsci.2006.10.013

DOI: 10.1021/ie9901630

DOI: 10.3844/ajassp.2012.784.793

DOI: 10.1021/am2012799

DOI: 10.1016/j.cocis.2015.11.00

DOI: 10.1016/j.petrol.2015.02.009


DOI: 10.1016/j.susc.2008.08.037

DOI: 10.1016/j.colsurfa.2015.09.048

DOI: 10.1021/am200861z

DOI: 10.1016/j.wear.2015.09.011

DOI: 10.1016/j.desal.2015.09.005

DOI: 10.1016/j.jcis.2012.05.040

DOI: 10.1016/j.carbon.2014.08.092

DOI: 10.1016/s0043-1354(01)00203-2

DOI: 10.1016/j.desal.2007.01.147

DOI: 10.1016/j.desal.2009.02.017


© 2018 Nkwoada et al.: This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history/23472